



Microscopic mechanism of perfluorocarbon gas formation in aluminum electrolysis process

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Abstract: In view of the unclear cause of perfluorocarbons (PFCs) emission in the anode effect stage of aluminum electrolysis, the microscopic formation mechanism of PFCs was studied by density functional theory calculation and X-ray photoelectron spectroscopy (XPS). It is found that the discharge of fluorine containing anions ($[F]^-$) on carbon anode first causes the substitution of C—H by C—F and further results in the saturation of aromatic C—C bonds, leading to the appearance of $-CF_3$ or $-C_2F_5$ group through six-carbon-ring opening. Elimination of $-CF_3$ and $-C_2F_5$ with F atom could be a likely mechanism of CF_4 and C_2F_6 formation. XPS results confirm that different types of $-CF_x$ group can be formed on anode surface during electrolysis, and the possibility that $[F]^-$ discharges continuously at the C edge and finally forms different C—F bonds in quantum mechanical calculation was verified.

Key words: microscopic formation mechanism; aluminum electrolysis; perfluorocarbon gas; density functional theory calculation

1 Introduction

Perfluorocarbons (PFCs), typically CF_4 and C_2F_6 [1], are substances that are closely related to global warming due to their high equivalent greenhouse effect, which is 6500–9200 times that of CO_2 [2,3]. Recent studies have confirmed that the aluminum electrolysis industry is the world's largest emission source of PFCs, accounting for about 90% of the total emission of PFCs [4,5]. Considering the huge primary aluminum output of China (57% of the world's total) and the developing trend of carbon emission reduction, controlling the emission of PFCs from aluminum electrolysis is very imperative [6].

Aluminum electrolysis is a complex electrochemical process involving multiple reactants and products. The electrolyte used in aluminum

electrolysis contains a variety of aluminum-fluoride and aluminum-oxy-fluoride anions [7,8], and each anion may discharge on the surface of carbon anode. In a normal electrolysis process, aluminum oxyfluoride coordination ions ($[O]^{2-}$) in molten salt discharge and react with carbon to produce CO_2 and CO [9,10]. However, because of the up-sizing of aluminum electrolytic cells (500–600 kA) for practical production, alumina concentration in the cell is inhomogeneous, which leads to frequent local anode effect [11,12]. It is widely accepted that the bubbles at the bottom of the anode would aggregate and thus hinder electric current passing through electrolysis to the anode when alumina concentration is consumed to the critical value, leading to the increase of cell voltage and further $[F]^-$ (aluminum–fluorine coordination ions in molten salt) discharge at the electrolyte/anode interface. As a consequence, PFC is formed and

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subsequently emitted in anode exhaust [13,14]. The anode gas generated during anode effect is composed of 2%–10% CO_2 , 70%–80% CO , 10%–20% CF_4 and 1%–3% C_2F_6 [15,16].

Though aluminum electrolysis technology is mature and has been applied for decades, the PFC formation mechanism during anode effect remains ambiguous. LEBER et al [17] and MARKS et al [18–20] found that the increase of voltage in anode effect would lead to PFC generation. TABEREAUX [21], and NISSEN and SADOWAY [22] commented that C_2F_6 formation only occurs in the early stage of anode effect. The generation rate and duration of C_2F_6 are much lower than CF_4 . QIN et al [23,24] declared that PFC emission increases with the increase of cell voltage during anode effect; however, it can still remain for an additional period after anode effect. ZHU and SADOWAY [25] detected four oxidation current peaks in anodic reaction and suggested the third current peak as the formation of graphite fluoride. Nevertheless, the electrode potential of C_2F_6 generation was not discussed. CHEN et al [26] observed different C—F bonds on the anode surface after electrolysis and considered this as an evidence of the existence of graphite fluoride. So far, more convincing evidence is needed to confirm the formation of graphite fluoride. The mechanism of PFC formation during aluminum reduction still deserves further investigation.

As for the formation mechanism of PFCs, at present, scholars mainly focus on experimental investigation, and theoretical exploration of micro formation mechanism is lacking. Therefore, in view of the unclear formation mechanism of PFCs and the lack of correlation between experiment and calculation, the combination of experiment and calculation is used to carry out the research. In this work, density functional theory (DFT) method is adopted to investigate the electrochemical reaction of fluorinated ions at the carbon anode/electrolyte interface [27,28]. The research experience in other fields shows that the chemical reaction process can be effectively simulated through molecular simulation and quantum chemical calculation, so as to describe the micro reaction process [29,30]. Meanwhile, laboratorial fluoride molten salt experiments are conducted to disclose electrode interface composition and bonding information. This work provides a theoretical basis for the

source emission reduction of smelting pollutants in industrial production.

2 DFT calculation and experiments

2.1 Theoretical assumptions

The formation of PFCs in aluminum electrolysis is a complex electro-chemical process, simultaneously involving multiple reactants, electron transfer and high temperature. So far, no direct theoretical method capable of simulating such process has been established. To apply DFT method to this study, we have proposed two assumptions.

(1) The discharge of $[\text{F}]^-$ on anode could be divided into three processes: the migration of $[\text{F}]^-$ from the middle of electrolyte to the surface of anode, the electron transfer from $[\text{F}]^-$ to anode, and the occurrence of C—F interaction on anode surface.

(2) The electric potential of carbon anode surface equals everywhere in a very local micro-area (atomic scale).

Through assumptions, it can be considered that the preponderant discharge position of $[\text{F}]^-$ on a very local anode surface could be estimated from the C—F bond energy.

2.2 Model structure

Pre-baked anode used in aluminum electrolysis is composed of multiple layers of irregularly stacked graphene. Consumption of carbon anode generally begins at the edges or surface defects of the monolayer of graphene. However, restricted by computation power, such complicated structure is hard to apply in quantum calculation. Hence, anode mode has been simplified in this study. The stack pattern of graphite layer is ignored given that it has little effect on chemical property of a very local structure.

Even though, several models should be investigated for their reactions in aluminum electrolysis. In this work, a typical single-layer small molecule aromatic fragment model (Model A) is used, as shown in Fig. 1(a). The C and H atoms related with reaction have been labeled for subsequent description, as shown in Fig. 1(b).

2.3 Calculation details

All DFT calculations were performed on the

Gaussian09D package [31]. All intermediates (IM) geometry optimization, frequency, and transition states (TS) were calculated at the B3LYP/6-311G++(d,p) level. Intermediates were confirmed with all real frequencies, and transition states were confirmed by only one imaginary frequency. Intrinsic reaction coordinate (IRC) [32] calculation was also employed to validate the connection between reactants and products. All energies reported herein were experienced by zero point energy (ZPE) correction.

To test the reliability of B3LYP/6-311G++(d,p), Model A was optimized at a variety of basis sets. The results are shown in Table 1.

From Table 1, it can be found that B3LYP/6-311G++(d,p), B3LYP/Def2-TZVP, M062x/cc-pVTZ and CBS-QB3 show nearly the same results on describing the geometry of Model A.

The strength of C—F interaction at different sites on the anode was estimated by the bond energy. Single F atom was selected as the reference in order to deduce the absolute energy. The discharge priorities of different $[F]^-$ ions will be discussed in our following work. The C—F bond energy ($E_{\text{bond energy}}$) is given by Eq. (1):

$$E_{\text{bond energy}} = E_{\text{product}} - (E_{\text{F atom}} + E_{\text{reactant}}) \quad (1)$$

where E_{product} is the total energy of C—F bonding product, $E_{\text{F atom}}$ is the energy of a fluorine atom, and E_{reactant} is the total energy of the reactant. Therefore, larger absolute value of $E_{\text{bond energy}}$ indicates stronger C—F bond.

In classical transition state theory, the reaction rate depends on the Gibbs free energy barrier (ΔG) at specific temperature. By comparing the Gibbs free energy barrier, the reaction rate can be qualitatively determined. On the basis of comparing the potential energy barrier ΔE at 0 K, we have further compared the Gibbs free energy barrier ΔG at 1250 K.

$$\Delta E = E_{\text{TS}} - E_{\text{reactant}} \quad (2)$$

$$\Delta G = G_{\text{TS}} - G_{\text{reactant}} \quad (3)$$

where the E_{TS} and G_{TS} are the potential energy and Gibbs free energy (1250 K) of transition state, respectively. E_{reactant} and G_{reactant} denote the potential energy and Gibbs free energy (1250 K) of reactant, respectively.

2.4 Molten salt experiment

High-purity graphite crucible was used as a reaction cell, and the reaction electrode was composed of high-purity graphite rod (Diameter $d=5$ mm). The bottom end of the exposed electrode

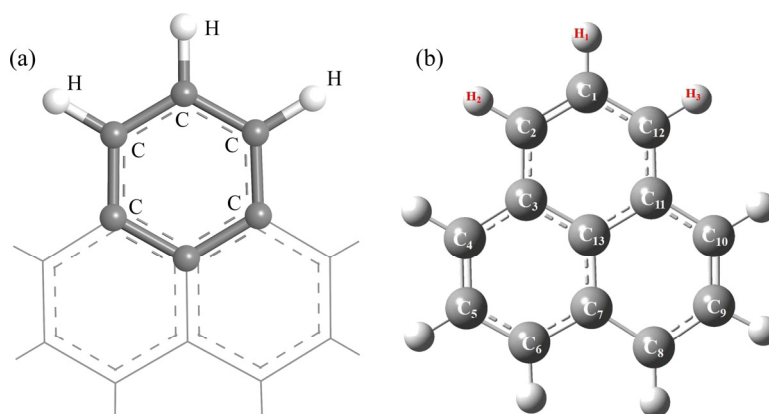


Fig. 1 Typical local edge structures of carbon anode Model A: (a) Schematic diagram of Model A; (b) Arrangement of C and H atoms in Model A

Table 1 Bond length and angle in Model A

Bond	Bond angle/(°)	Bond length/Å			
		B3LYP/6-311++G(d,p)	B3LYP/Def2-TZVP	M062x/cc-pVTZ	CBS-QB3
C ₁ —C ₂	120.78	1.391	1.387	1.384	1.390
C ₂ —C ₃	120.77	1.417	1.414	1.411	1.417
C ₃ —C ₁₃	120.74	1.429	1.426	1.421	1.429
C ₁ —H ₁	120.79	1.085	1.083	1.082	1.084

was dipped into the molten salt and used as the reaction interface. 550 g of uniform reactant mixture which consists of NaF (54.8 wt.%) + AlF_3 (44.7 wt.%) + Al_2O_3 (0.5 wt.%) was used as the electrolyte. Alumina was analytically pure and cryolite was synthetic one. The required reagent was placed in a drying oven to dry for 24 h before the experiment. A self-made well furnace equipped with a CW-3100 temperature controller and an MPS705 DC (0–60 V and 0–20 A) steady current and voltage supply was used. The electrolysis temperature was 1250 K. The constant current was 1.5 A/cm^2 . The electrolysis duration was 2 h. The anode was removed from the electrolyte before electricity black-out to minimize the adhesion of the electrolyte to the surface of the anode. The surface of the electrolyzed graphite anode was cut after air cooling. The sample surface was analyzed by X-ray photoelectron spectroscopy (XPS), in order to obtain the chemical valence states of each element.

3 Results and discussion

3.1 Quantum chemical calculation results

3.1.1 Initial reaction steps of Model A

Prior to the illustration of PFC formation, the

reactions related with H atoms in Model A need to be illustrated. The C—F bond energies at different positions have been calculated to evaluate the discharge sequence of $[\text{F}]^-$ in Model A. Results are shown in Table 2.

Table 2 Potential energy ΔE and Gibbs free energy change ΔG (1250 K) of C—F bond at different positions

Position	$\Delta E/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta G/(\text{kJ}\cdot\text{mol}^{-1})$
$\text{C}_1\text{—F}$	−285.60	−125.65
$\text{C}_2\text{—F}$	−285.56	−125.56
$\text{C}_{13}\text{—F}$	−112.21	47.45

From Table 2, it can be seen that both the ΔE and ΔG (1250 K) of C—F bond at C_1 site are much lower than those at other sites. This indicates that $[\text{F}]^-$ is more likely to discharge and form anode chemically absorbed F (F_{anode}) at the edge of aromatic fragment. Elimination of H atom is through combination with F_{anode} . Potential energy surface (PES) of the H atom elimination process is shown in Fig. 2. The energy above the horizontal line represents the relative energy at 0 K, and the energy in brackets below the horizontal line is the relative energy at 1250 K.

For the process of Original to I3, $[\text{F}]^-$ discharges

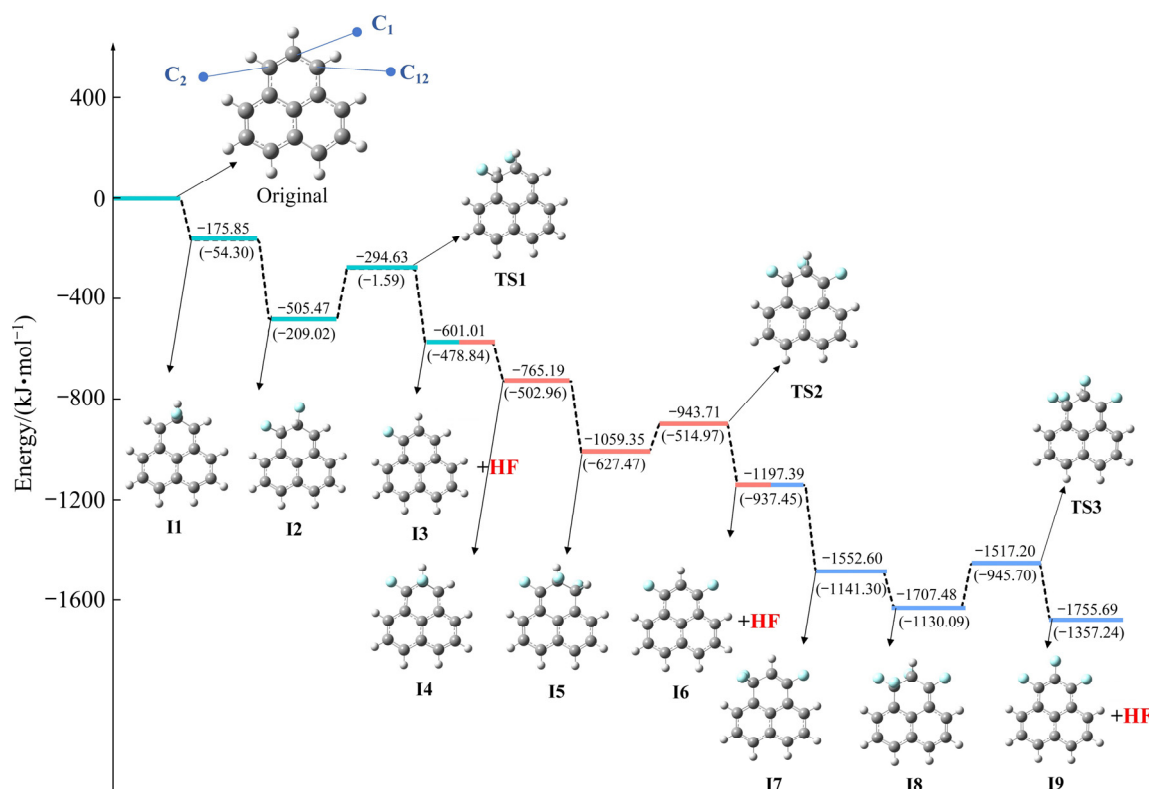


Fig. 2 PES of H atom elimination process

at C_1 and C_2 positions stepwise, leading to formation of C_1-F_1 and C_2-F_2 bonds, respectively. Following, the interaction of F atom (C_1 position) with the H atom (C_2 position) gives a HF molecule and thus leads to I3 intermediate. The potential energy barrier of the HF formation from I2 is 210.83 kJ/mol. Subsequently, $[F]^-$ discharges on the newly generated I3 structure to form I5 at C_1 and C_{12} positions stepwise, which could be transformed to I6 and HF via C_1-F interaction accompanied with $C_{12}-H_3$ bond cleavage and $F-H_3$ bond formation. The potential energy barrier of this process is 115.65 kJ/mol. Likewise, the reaction of I6–I9 is analogy to RE–I5 process. The potential energy barrier of the HF formation from I8 is 190.29 kJ/mol. Thus, the original H atoms are replaced by F bonds through six $[F]^-$ discharges.

3.1.2 CF_x formation

For intermediate I9, the discharge of $[F]^-$ would lead to ring opening and thus three $-CF_x$ chain groups are generated. Details of this process are demonstrated in Fig. 3.

The stepwise discharge of $[F]^-$ at C_2 , C_{12} , C_1 and C_{11} positions leads to the formation of C_2-F_1 , $C_{12}-F_2$, C_1-F_3 and $C_{11}-F_4$ bonds, respectively. Three ring opening pathways for IM3 have been identified. Via transition state TS4, IM4 is obtained

through C_1-C_{12} bond cleavage. The opening of the six-carbon ring leads to a $-C_2F_5$ chain. The potential energy barrier of this process at 0 K is 382.17 kJ/mol, and Gibbs free energy barrier at 1250 K is 367.82 kJ/mol. Besides, IM5 is converted from IM3 via transition state TS5 by overcoming a potential energy barrier of 361.37 kJ/mol (Gibbs free energy barrier is 345.01 kJ/mol). The ring opening causes the formation of $-C_3H_7$ group. Additionally, IM3 could transform to IM6 via transition state TS4 by $C_{11}-C_{12}$ bond cleavage, resulting in another $-C_3H_7$ group. The potential energy barrier of this process is 348.11 kJ/mol (Gibbs free energy barrier is 1146.92 kJ/mol).

It can be deduced that the formation of IM6 is favored over other intermediates by comparing potential energies. However, when the temperature rises to 1250 K, the Gibbs free energy barrier of IM6 is the largest, which is difficult to generate. Relatively speaking, IM4 is very thermodynamically stable. The three intermediates are supposed to co-exist during PFC formation. In the following, the PFC formation from IM4, IM5 and IM6 will be discussed.

3.1.3 PFC formation from IM5 and IM6

IM5 could be converted into IM10 and undergo 8 pathways. Details of these pathways have

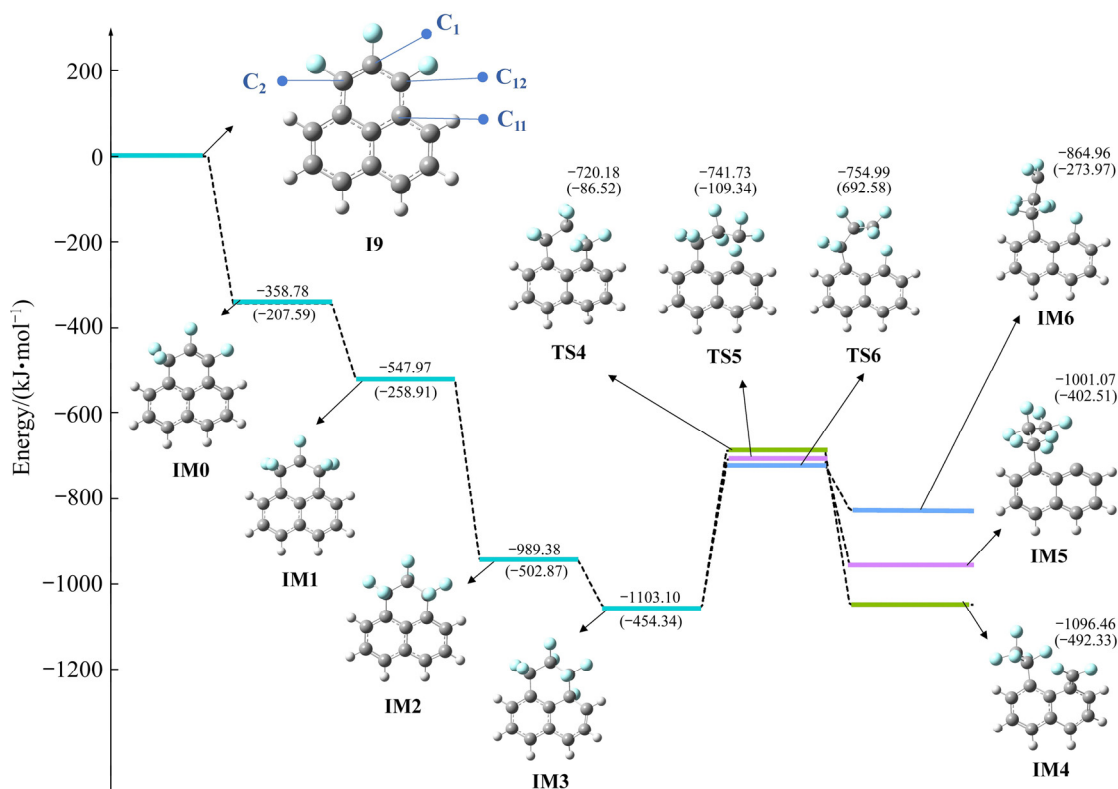


Fig. 3 PES of I9 reactions

been illustrated in Fig. 4 and Fig. 5. For IM6 and IM5 pathways cross at IM10 intermediate, Fig. 4 also contains the reaction pathway of IM6. The PES of Pro1 + CF₄ and Pro2 + C₂F₆ formation pathways can be found in Fig. 4.

IM10 can be converted from IM5 by discharge of two [F][−] anions at C₁₁ position, leading to C₁₁—F₁ and C₁₁—F₂ bond formation. Alternatively, IM10 can also be generated from IM6. Specifically, the [F][−] discharge at C₁₂ position of IM6 forms IM7. Following, IM8 is formed from IM7 by C₁₂—F bond crack and C₁₁—F bond formation via TS7 (The potential energy barrier is 508.19 kJ/mol). Another [F][−] discharge at C₁₂ site of IM8 forms IM10. Considering the potential energy barrier in IM6–IM10 pathway, pathway of IM5–IM10 is considered to be favored.

Pro1 + CF₄ can be formed from IM10 by C₁₂—C₁, C₁₁—F₁ bond cleavage and C₁₂—F₁ bond formation via transition state TS8. The potential energy barrier is 438.02 kJ/mol. Meanwhile, Pro2 + C₂F₆ can be produced from IM10 via transition state TS9 through C₁—C₂ and C₁₁—F₂ cleavage accompanied with C₁—F₂ formation. The potential energy barrier is 390.20 kJ/mol.

IM9 and IM10 could undergo additional pathways to form another four products. Details can be found in Fig. 5.

The discharge of [F][−] at C₁₀ site of IM9 forms IM10, as shown in Fig. 4. Whereas, the [F][−] discharge at C₁₃ position of IM9 forms IM13. From IM13, two possible intermediates, IM14 and IM15, could be formed via [F][−] discharge at C₃ and C₁₃ positions. Three possible pathways for IM14 to generate PFC have been found. The first path is the cleavage of C₁—C₁₂, forming —CF₃ group. The interaction of F atom (C₁₃ position) with the —CF₃ group gives a CF₄ molecule and thus leads to product Pro4. The second path is the cleavage of C₂—C₃, resulting in —C₃F₇ group. The interaction of F atom (C₂ position) with the —C₃F₇ group forms a C₃F₈ molecule and thus leads to Pro5. The third path is to convert to IM16 via [F][−] discharge at C₁₂ site. The following cleavage of C₁—C₂ forms —C₂F₅ group. Pro6 (C₂F₆) is produced through the elimination of F atom (C₁ position) with the —C₂F₅ group.

For IM15, two possible reaction paths have been identified. Via transition state TS10, Pro3 + CF₄ is generated by C₁—C₁₂ and C₁₃—F₁

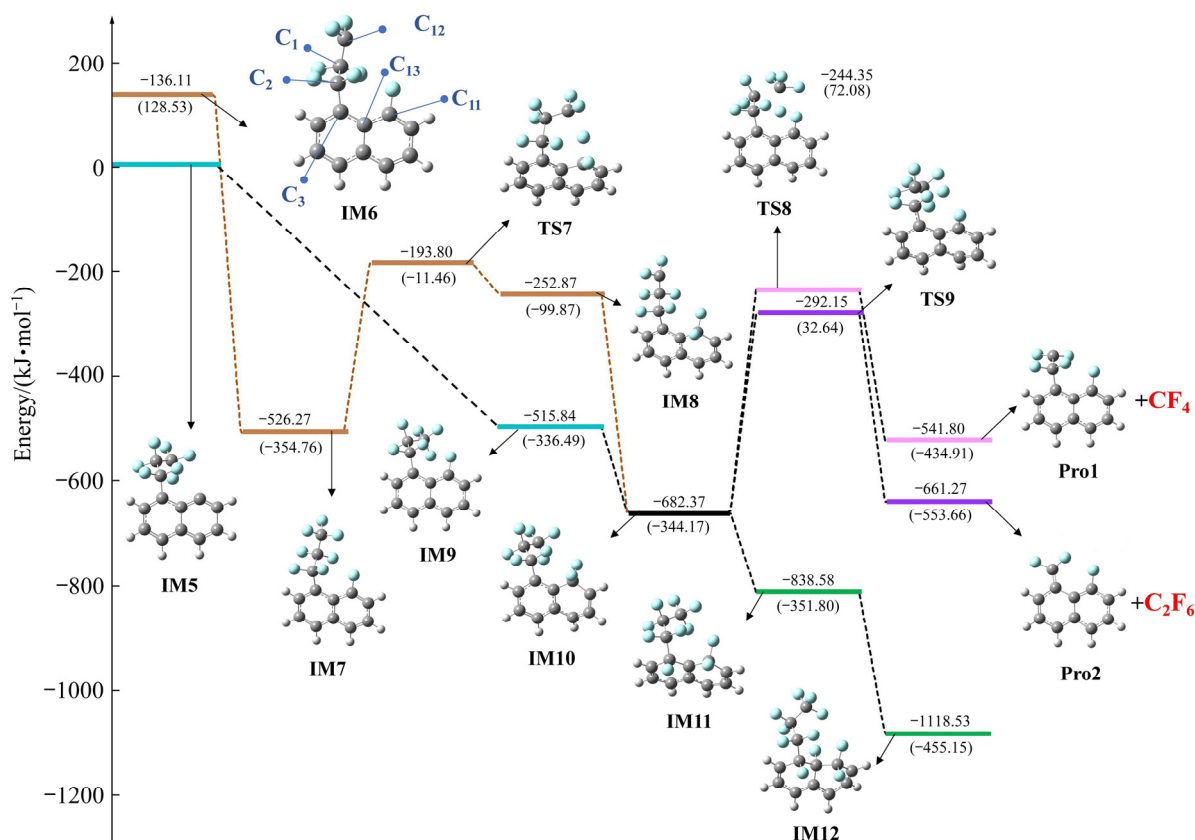


Fig. 4 PES of IM5 and IM6 reaction pathways

cleavage accompanied with $C_{12}-F_1$ formation. The potential energy barrier of this step is 415.68 kJ/mol. Additionally, $[F]^-$ discharge at C_3 position of IM15 forms IM12. Then, IM12 dissociates to $Pro6 + C_2F_6$ via TS13 by C_1-C_2 and $C_{13}-F_2$ cleavage accompanied with C_1-F_2 formation. The potential energy barrier is 418.73 kJ/mol.

There are five possible paths to produce the final product, the potential energy barrier appears in the process of forming $-CF_3$, $-C_2F_5$ and $-C_3F_7$ groups. The maximum potential barrier and maximum Gibbs free energy barrier of each pathway are listed in Table 3. It can be seen that $Pro5 + C_3F_8$ is relatively easy to be generated.

3.1.4 IM4 reaction process

PES of the reaction path of IM4 is shown in Fig. 6.

The discharge of $[F]^-$ at C_3 and C_{13} sites of IM4 results in IM20. Depending on the discharge sequence of C_3 and C_{13} sites, two competitive intermediates, IM17 and IM18, could be converted. Judging from the potential energy and the Gibbs free energy, IM18 is more favorable than IM17. Via transition state TS17, $Pro7 + C_2F_6$ can be formed through $-C_2F_5$ group combining with the additional absorbed F atom. The potential energy barrier of this process is 238.24 kJ/mol.

Notably, two intermediates, IM21 and IM22, could be formed in IM4 reactions. Besides, there are two possible paths to produce IM21. Firstly, the discharge of $[F]^-$ at C_{13} forms IM18, which could be converted to IM21 via TS16 by F atom migration from C_{13} to C_{12} site. The potential energy barrier of this step is 77.15 kJ/mol. In the other route, IM21

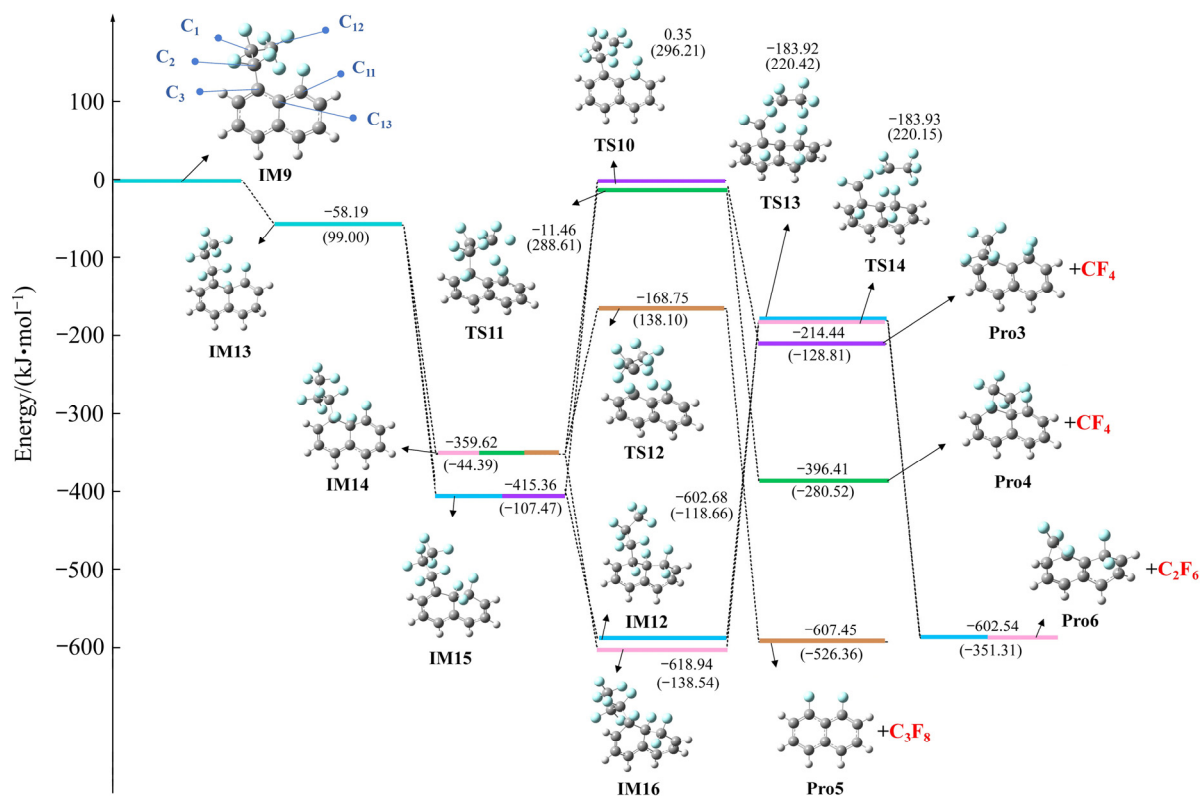


Fig. 5 PES of IM9 reaction pathways

Table 3 Maximum potential energy barrier $\Delta_{\max}E$ and Gibbs free energy barrier $\Delta_{\max}G$ (1250 K) of IM9 reaction pathways

Final product	Reaction path	$\Delta_{\max}E/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta_{\max}G/(\text{kJ}\cdot\text{mol}^{-1})$
Pro3+CF ₄	IM9→IM13→IM15→TS10→Pro3+CF ₄	415.68	403.71
Pro4+CF ₄	IM9→IM13→IM14→TS11→Pro4+CF ₄	348.15	333.00
Pro5+C ₃ F ₈	IM9→IM13→IM14→TS12→Pro5+C ₃ F ₈	190.87	182.51
Pro6+C ₂ F ₆	IM9→IM13→IM14→IM16→TS14→Pro6+C ₂ F ₆	435.01	358.69
	IM9→IM13→IM15→IM12→TS13→Pro6+C ₂ F ₆	418.73	339.07

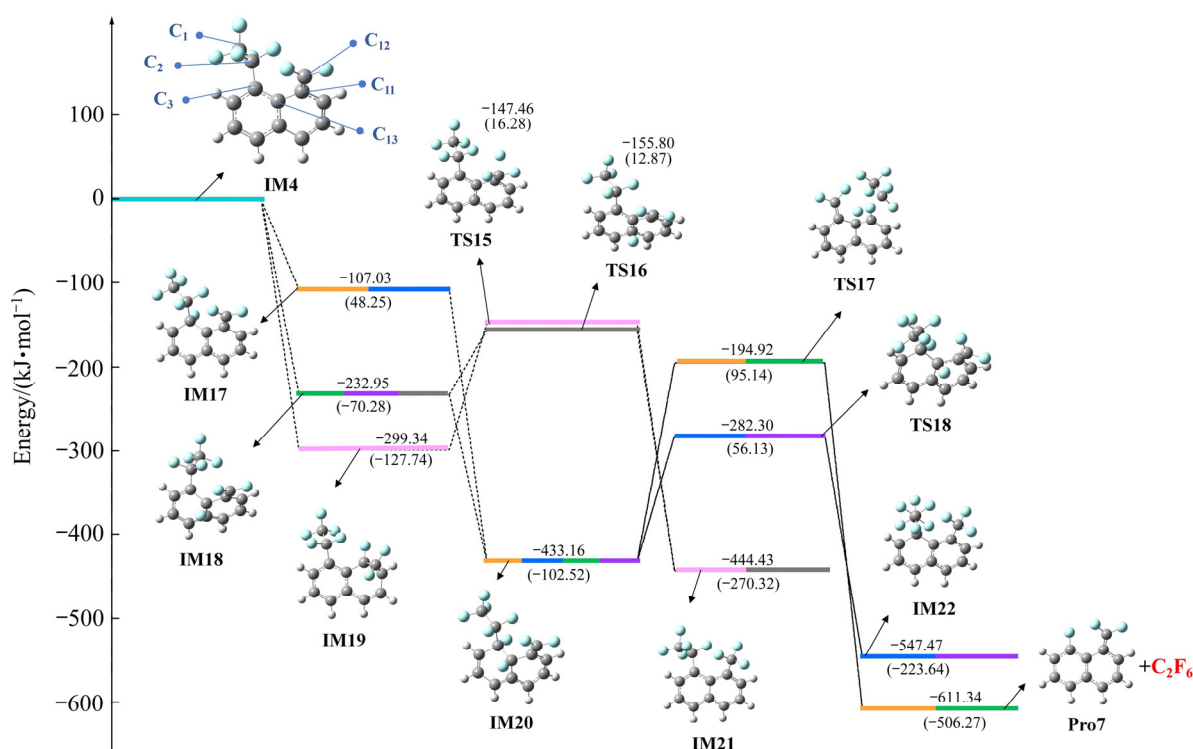


Fig. 6 PES of IM4 pathways

is formed by IM19 via TS15 by F atom migration. The potential energy barrier is 151.88 kJ/mol. There are also two possible paths to form IM22. IM22 is converted from IM20 via transition state TS18 by the migration of F from C₁₃ site to C₁₂ site. The potential energy barrier is 238.24 kJ/mol. IM22 could also be generated from IM21 by [F]⁻ discharge at C₃ site. PES of IM21 reaction pathways are illustrated in Fig. 7.

Three possible paths for further reaction of IM21 have been found. Pro8 + CF₄ is generated from IM21 via transition state TS19 through C₁—C₂ and C₁₂—F₁ cleavage accompanied with C₁₃—F₁ and C₂—C₃ formation. The potential energy barrier is 514.63 kJ/mol. The second path is via the discharge of [F]⁻ at C₁ and C₁₃ positions of IM21, leading to the formation of IM23 and IM25 stepwise. Then, the cleavage of C₁₂—C₁₁ gives a —CF₃ group and the interaction of F atom (C₁₃ position) with the —CF₃ group forms a CF₄ molecule. The potential energy barrier is 220.83 kJ/mol. The third path is via the stepwise discharge of [F]⁻ at C₃ and C₁₃ sites, leading to the formation of IM22 and IM24, respectively. Finally, the cleavage of C₂—C₃ bond causes ring opening and thus forms a —C₂F₅ group. Interaction of F atom (C₁₃ position) with the —C₂F₅ group gives a

C₂F₆ molecule. The potential energy barrier is 181.33 kJ/mol.

For the three reaction paths, the energy barrier appears in the process of forming —CF₃ or —C₂F₅ group, therefore, the elimination step of —CF₃ or —C₂F₅ is the rate-limiting step. From the aspect of the Gibbs free energy barrier, the third reaction pathway is more likely to take place.

3.1.5 Further reactions of Pro8 and Pro10

We have also found that the products above possibly undergo further reactions by [F]⁻ discharge. In this section, further reactions of Pro8 and Pro10 will be discussed. PES of IM8 reaction path is presented in Fig. 8.

Firstly, [F]⁻ discharges at C₁ position of Pro8, leading to the formation of C₁₁—F bond. Then, Pro8 transforms into IM26. IM27 can be produced from IM26 via transition state TS22 through C₂—C₁₂ and C₁₁—F cleavage accompanied with C₁₂—F formation. The potential energy barrier is 349.95 kJ/mol. Then, [F]⁻ discharges at C₂, C₁₁ and C₃ positions stepwise to form IM28, IM29 and IM30. IM31 is generated through C₃—F₁ cleavage accompanied with C₁₃—F₁ formation via transition state TS23. The potential energy barrier is 55.48 kJ/mol. Subsequently, the cleavage of C₁₂—C₁₁ bond forms a —CF₃ group. Finally, CF₄

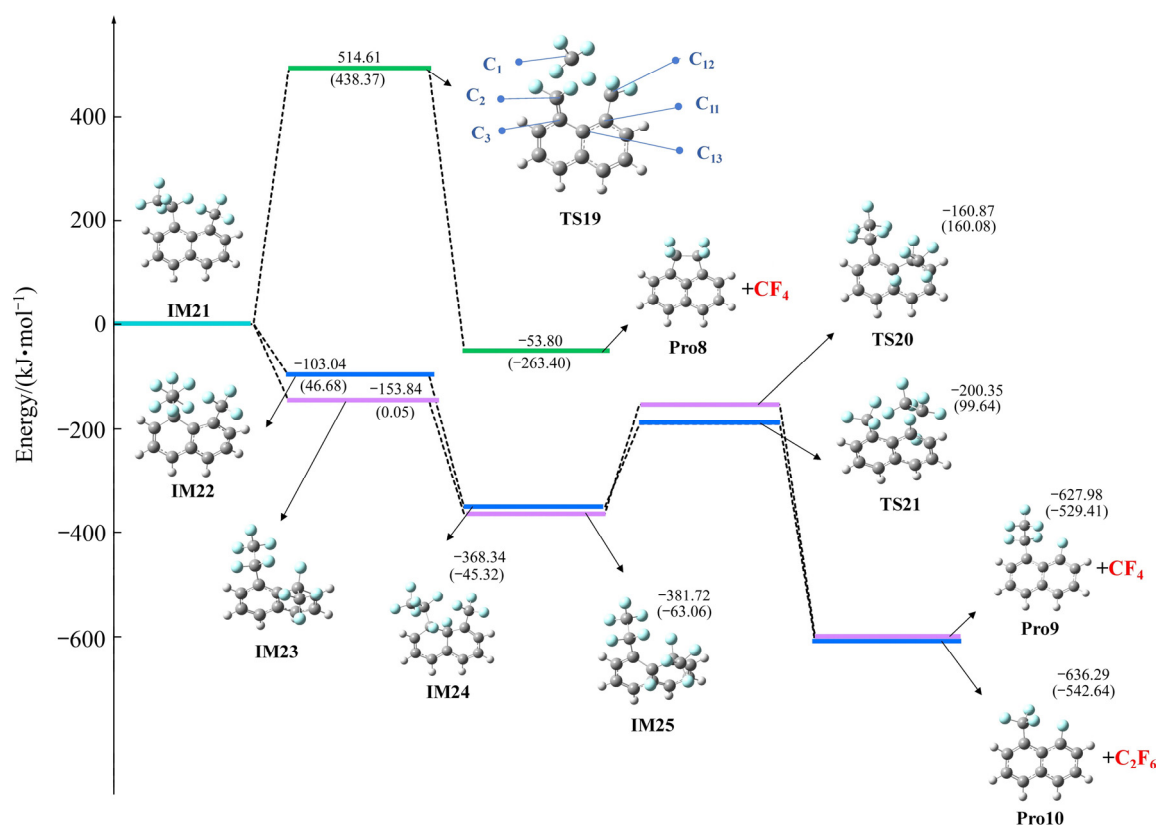
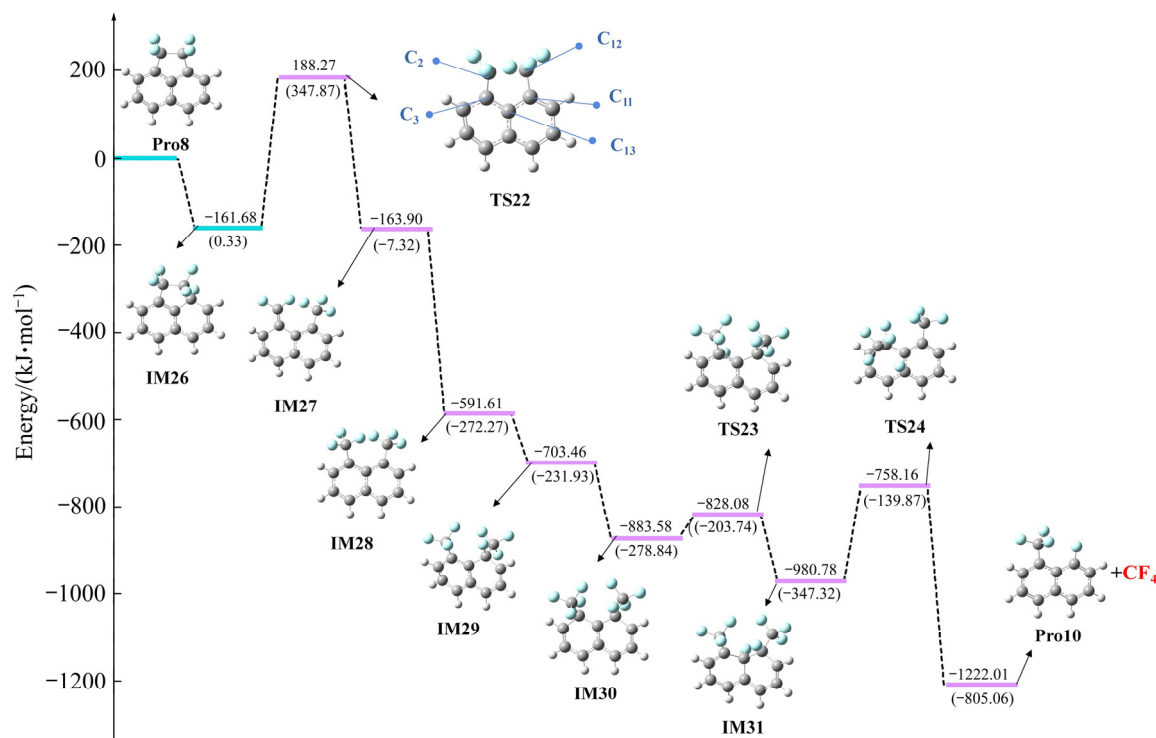


Fig. 7 PES of IM21 pathways

Fig. 8 PES of Pro8 transforming into product Pro10 + CF₄

is obtained via the interaction of F atom (C₁₃ position) with the —CF₃ group. The potential energy barrier is 221.63 kJ/mol.

From Pro8 to Pro10 + CF₄, the highest potential energy barrier is 349.95 kJ/mol in the IM26–IM27 process. It shows that the decisive step

in the whole reaction process is the opening of carbon ring caused by the cleavage of C—C bond.

Pro5 + C₂F₆ could also be produced from Pro8. The PES of reaction path is shown in Fig. 9.

IM26 can be formed from Pro8 via [F][−] discharge at C₁ position. IM32 is then converted via transition state TS25 through carbon ring opening at C₁₂—C₁₁. The potential energy barrier of this process is 130.25 kJ/mol. The following discharge of [F][−] at C₁₁ position forms IM33. IM34 is produced via transition state TS26 through C₁₁—F cleavage accompanied with C₁—F formation. The potential energy barrier is 1.88 kJ/mol. Subsequently, [F][−] discharges at C₁₃ and C₃ positions and thus forms IM35 and IM36. The cleavage of C₂—C₃ bond of IM36 generates a —C₂F₅ group. Through F atom (C₁₃ position) interaction with the —C₂F₅ group, C₂F₆ is finally produced. The potential energy barrier is 203.26 kJ/mol.

From Pro8 to Pro5 + C₂F₆, the highest potential energy barrier is 203.26 kJ/mol in the process from IM36 to Pro5 + C₂F₆. It shows that the speed determining rate step in the whole reaction process is the breaking of C—C bond, resulting in the stripping of —C₂F₅ group.

Another pathway for IM26 is shown in Fig. 10.

By two the discharge of [F][−] at C₁₃ and C₃ sites of Pro10, IM38 can be converted. Pro5 + CF₄ is then formed via transition state TS28 by the elimination of —CF₃ with another F atom. The potential energy barrier of this step is 222.84 kJ/mol.

It is suggested that the three H atoms connected to the three C atoms (C₁, C₂ and C₁₂) of benzene ring are firstly substituted by F atom and then saturated by chemically absorbed F atom, and finally transformed into —C_xF_y group via ring opening. CF₄ and C₂F₆ molecules are formed via the elimination of —C_xF_y group with additional chemically absorbed F atom. Hence, PFC formation needs multiple F atom participation.

3.2 Molten salt experiment results

The high-resolution C 1s and F 1s XPS spectra of Sample A were fitted and analyzed by Thermo Avantage software to obtain the detailed chemical valence and structure information of the anode surface. The fitting results are shown in Fig. 11.

It can be seen from Fig. 11(a) that the C 1s contains 7 component peaks. The two strongest component peaks C₁ and C₂ are C sp², which is the main component in graphite, with a binding energy of 284.45 and 284.72 eV, respectively. C₃, with a binding energy of 284.82 eV, is C sp³ that can be

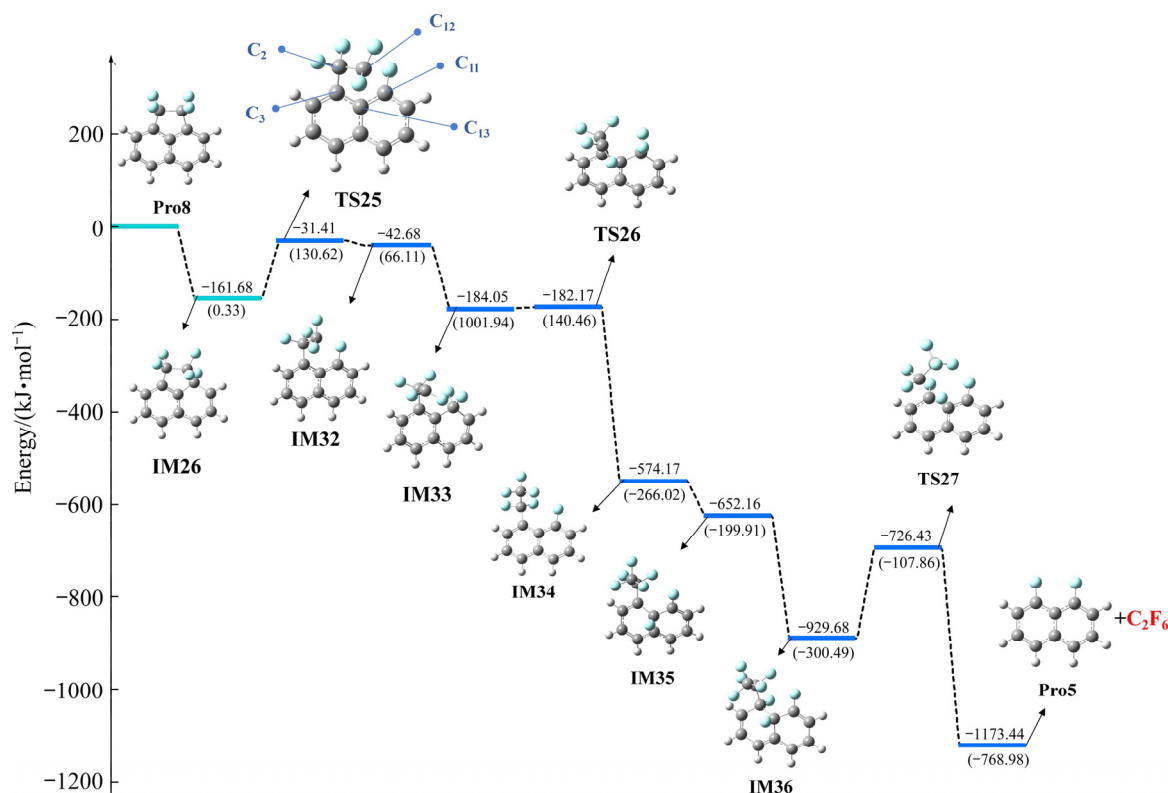


Fig. 9 PES of Pro8 transforming into product Pro5 + C₂F₆

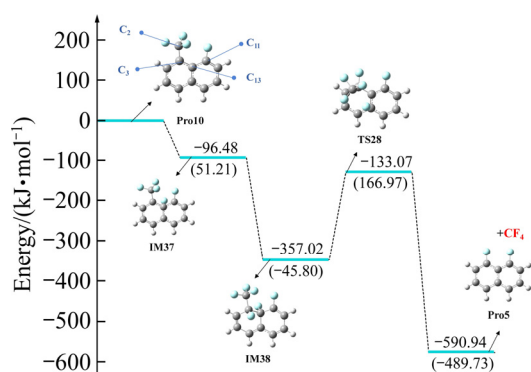


Fig. 10 PES of Pro10 pathway

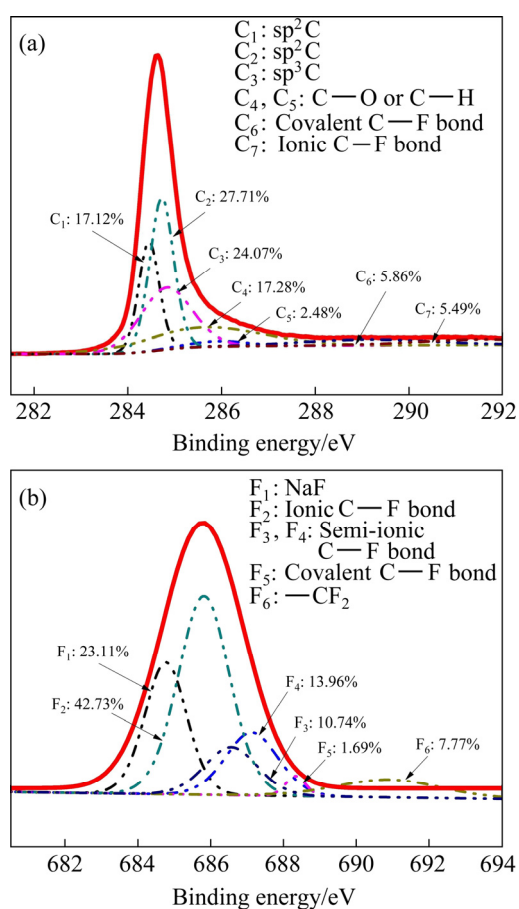


Fig. 11 High-resolution C 1s (a) and F 1s (b) XPS spectra of Sample A

assigned to a nonfunctional graphite aromatic ring. The binding energies of C₄ and C₅ peak sites are 285.62 and 285.91 eV, which should be corresponding to the C—O and C—H structures, respectively. C 1s peaks with binding energies higher than 289 eV are fluorinated covalent C—F bond (C₆) and ionic C—F bond (C₇). The F 1s also contains 6 component peaks (Fig. 11(b)). Except for the NaF component peak of F₁ with binding energy of 684.77 eV, the other five component peaks are all

C—F bonds. The F₂ with binding energy of 685.82 eV is ionic C—F bond [33]. The binding energies of F₃ and F₄ at 686.57 and 687.13 eV represent the semi-ionic C—F bond, respectively. F₅, which has a binding energy of 688.33 eV, is a covalent C—F bond. The content of F₅ is very low. The binding energy of F₆ is 690.90 eV, which indicates a —CF₂ structure.

By adjusting the voltage to induce anode effect in molten salt electrolysis experiment, the composition and relative content of F element in each chemical state of Sample A were analyzed. It was found that when the anodic potential reached the [F][−] discharge potential, C—F bonds that represent different structural forms were detected on the anodic surface after electrolysis, and there were semi-ionic C—F bond, ionic C—F bond, covalent C—F bond, and —CF₂ bond. The proportion of C—F bond in Sample A is roughly: ionic C—F bond (42.73%), semi-ionic C—F bond (24.7%), covalent C—F bond (1.69%), and —CF₂ (7.77%). After electrolysis, C—F bonds of different structural forms were detected on the anode surface, which is in accordance with the results of first-principles calculations. This proves that there would be different forms of C—F bonds generated during the process of [F][−] discharge. The [F][−] will continue to discharge on the anode surface, and eventually break the bond to form the products CF₄ and C₂F₆.

4 Conclusions

(1) The discharge of fluorine containing anions ([F][−]) on carbon anode may lead to the saturation of aromatic rings, resulting in the formation of —CF₃ or —C₂F₅ groups via ring opening. The subsequent elimination of —CF_x groups with additional F atom can generate PFC.

(2) Compared with CF₄ formation, higher potential energy barrier and Gibbs free energy barrier have been located in C₂F₆ formation path. It is partially indicated that CF₄ is favored in aluminum electrolysis exhaust, which is consistent with industry situation. However, more structure models are needed to be investigated in following work.

(3) The XPS analysis indicates that different —CF and —CF₂ exist on the carbon anode surface after laboratorial electrolysis. This is in good

agreement with the DFT calculations that PFC could be directly converted from $-\text{CF}_x$ groups.

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铝电解全氟化碳气体的微观形成机理

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摘 要: 针对目前铝电解阳极效应阶段全氟化碳(PFCs)气体排放原因不明的问题, 采用密度泛函理论计算与 X 射线光电子能谱(XPS)检测手段对 PFCs 的微观形成机理进行研究。计算结果表明, 在阳极表面不断放电的过程中, 熔盐中含氟配离子[F⁻]使碳环边缘的 C—H 键逐渐被 C—F 键取代, 导致芳香族 C—C 键饱和, 随后碳环开环逐渐形成—CF₃基团和—C₂F₅基团, 最终脱出 CF₄和 C₂F₆产物。XPS 结果表明, 电解后的阳极表面存在不同类型的—CF_x结构, 验证了量子力学计算中[F⁻]在碳边缘不断放电、最终形成不同 C—F 键的可能性。

关键词: 微观形成机理; 铝电解; 全氟化碳气体; 密度泛函理论计算

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